

# The Use of Field Deployable Instrumentation for the Monitoring of Munitions Constituents in Groundwater

David Splichal, Anthony Bednar, Amber Russell,  
Tom Georgian, Charolett Hayes, Louise Parker,  
Robert Kirgan, Mitch Wells

March 2011



US Army Corps of Engineers  
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Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE <b>31 MAR 2011</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2011 to 00-00-2011</b>	
4. TITLE AND SUBTITLE <b>The Use of Field Deployable Instrumentation for the Monitoring of Munitions Constituents in Groundwater</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>US Army Corps of Engineers,Environmental Laboratory,3909 Halls Ferry Road,Vicksburg,MS,39180-6199</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>Presented at the 2011 DoD Environmental Monitoring &amp; Data Quality Workshop (EMDQ 2011), 28 Mar ? 1 Apr, Arlington, VA.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>19</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

# Introduction

- Long Term Monitoring of Groundwater
  - ▶ Can be required for 30+ years
    - Long after activities at a site have ceased
  - ▶ Regulatory approved methods/detection limits
  - ▶ Laborious and expensive process
    - Sample collection, overnight shipment under COC
      - ▷ Over \$160/cooler shipping costs alone
    - Fixed laboratory analysis can be slow and expensive
      - ▷ 30-60 days, \$225/sample for explosives
- Field analysis goals
  - ▶ Rapid (near real time)
  - ▶ Cheaper (no shipment costs)
  - ▶ Comparable results
    - Absolute detection, confirmation, and quantitation
  - ▶ NB, 1,3-DNB, 2,4-DNT, TNB, TNT, RDX
  - ▶ Demonstrated at 2 field sites, Louisiana and Milan AAPs





# Deployable Mass Spectrometer

## Field Extraction Equipment



## ICx Griffin 400 and 450



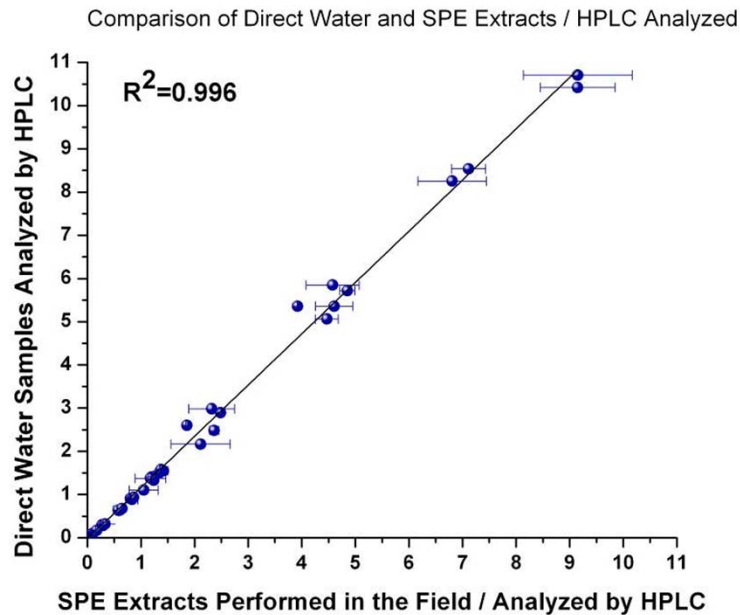
Field Portable = Minimal support services, i.e. power from a 5 kW generator, instrumentation fits in the same 4 m trailer the groundwater sampling supplies are transported in.

GC-MS is approximately 2' cube, weighs 35 kg



# Field Extraction Methods

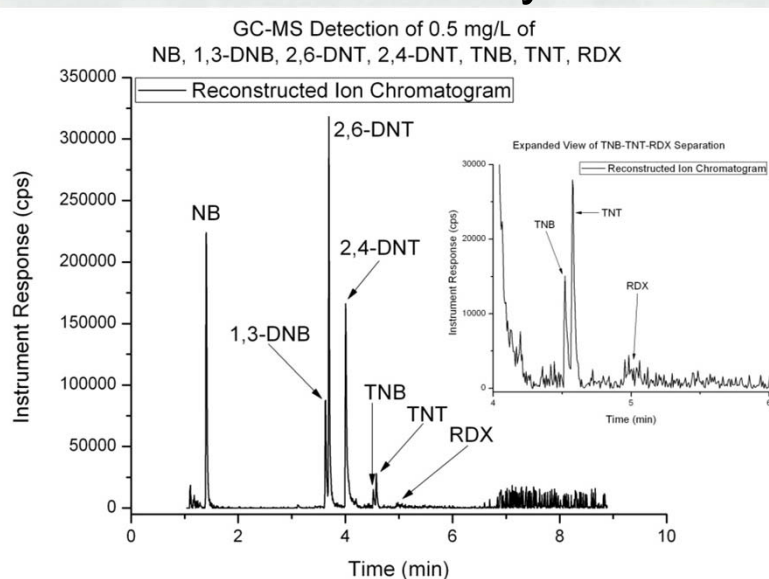
- Solid Phase Extraction Cartridges
  - ▶ Method 3535A
  - ▶ Compared to direct water analysis (values in ppm)
  - ▶ Same analytical method, HPLC, 8330B





# Field Instrument Performance

- Instrument calibration range (SIM) 0.3 – 2.5 mg/L
  - ▶ Ground water concentration range 1.5 – 12.5  $\mu\text{g/L}$  (CF of 200)
  - ▶  $R^2 > 0.95$  for all analytes
  - ▶ Quantitation limit 1  $\mu\text{g/L}$
  - ▶ Yields an effective analysis at 2  $\mu\text{g/L}$  with SPE extraction concentration factor ( $\sim 200\times$ )
  - ▶ Time from analysis to data reporting is  $\sim 9$  minutes



Analyte	MDL	0.001 ppm Verification	% REC
NB	0.0026	0.0012	120.0
1,3-DNB	0.0005	0.0011	110.9
2,4-DNT	0.0006	0.0008	75.8
TNB	0.0003	0.0005	52.2
TNT	0.0003	0.0013	133.2
RDX	0.0016	0.0012	117.0



# Field Instrument LCS Recoveries

	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
<b>DoD QSM Limits</b>	50-140	45-160	60-135	65-140	50-145	50-160
<b>LAAP Day 1</b>	78	73	82	83	74	57
<b>LAAP Day 2</b>	58	47	60	73	59	<b>33</b>
<b>LAAP Day 3</b>	110	65	96	91	83	69
<b>MAAP Day 1</b>	100	98	91	81	82	55
<b>MAAP Day 2</b>	110	93	100	72	67	<b>41</b>
<b>MAAP Day 3</b>	99	100	110	<b>62</b>	70	57
<b>MAAP Day 4</b>	77	110	100	79	88	110

LCS spike concentration 10 µg/L



# Field Instrument MS Recoveries

	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
<b>DoD QSM Limits</b>	50-140	45-160	60-135	65-140	50-145	50-160
<b>LAAP Day 1</b>	96	86	91	74	63	<b>45</b>
	100	74	120	100	92	<b>38</b>
<b>LAAP Day 2</b>	92	<b>180</b>	<b>170</b>	<b>7000</b>	<b>3600</b>	<b>-2200</b>
	99	<b>240</b>	<b>200</b>	<b>5300</b>	<b>2200</b>	<b>-3800</b>
<b>LAAP Day 3</b>	80	72	73	75	72	54
	96	100	93	88	81	<b>49</b>
<b>MAAP Day 1</b>	120	110	110	66	55	<b>9.8</b>
	120	77	96	79	58	<b>26</b>
<b>MAAP Day 2</b>	110	68	100	<b>59</b>	54	<b>260</b>
	120	99	120	89	81	<b>200</b>
<b>MAAP Day 3</b>	<b>160</b>	110	110	<b>22</b>	61	<b>20</b>
	140	93	110	<b>23</b>	66	<b>37</b>
<b>MAAP Day 4</b>	70	99	94	66	86	<b>33</b>
	98	130	100	76	96	<b>34</b>





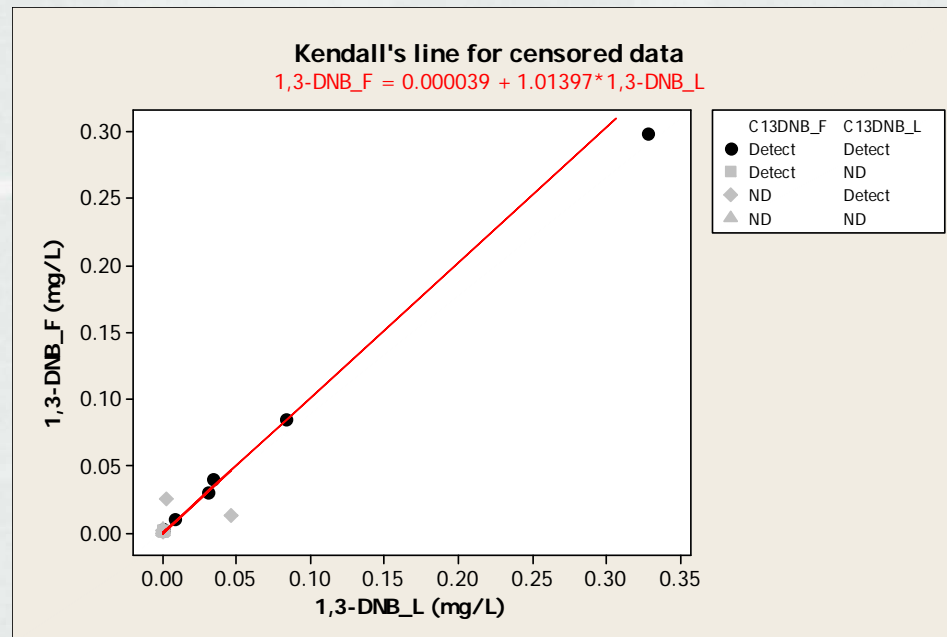
# Laboratory-Field Comparison

- 28 groundwater samples collected from LAAP and MAAP
  - ▶ Additional 'synthetic groundwater' samples created by dilution of elevated samples with clean groundwater to make water samples with lower concentrations in a natural matrix
- Nitrobenzene (NB) was not detected in any groundwater sample by the field or laboratory methods
  - ▶ Limited comparison, but no false positives or negatives for the matrices tested



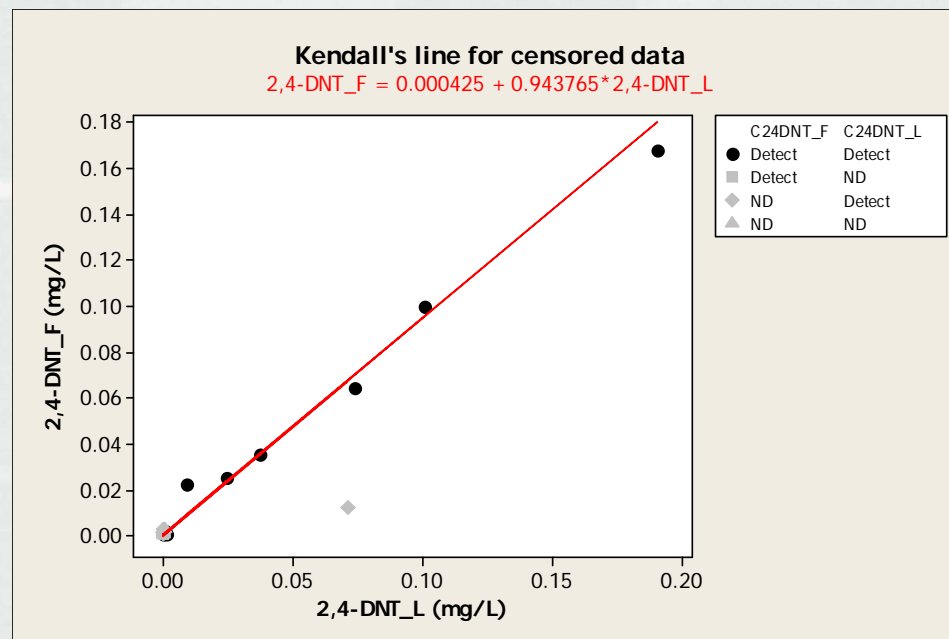
# Laboratory-Field Comparison

- 1,3-DNB results show excellent agreement
  - ▶ Limited concentration range and dataset due to several non-detects
  - ▶ Ordinary least squares fit:  $F = 0.86L + 0.018$
  - ▶ Kendall-Theil (K-T) Line:  $F = 1.0 L + 0.00039$



# Laboratory-Field Comparison

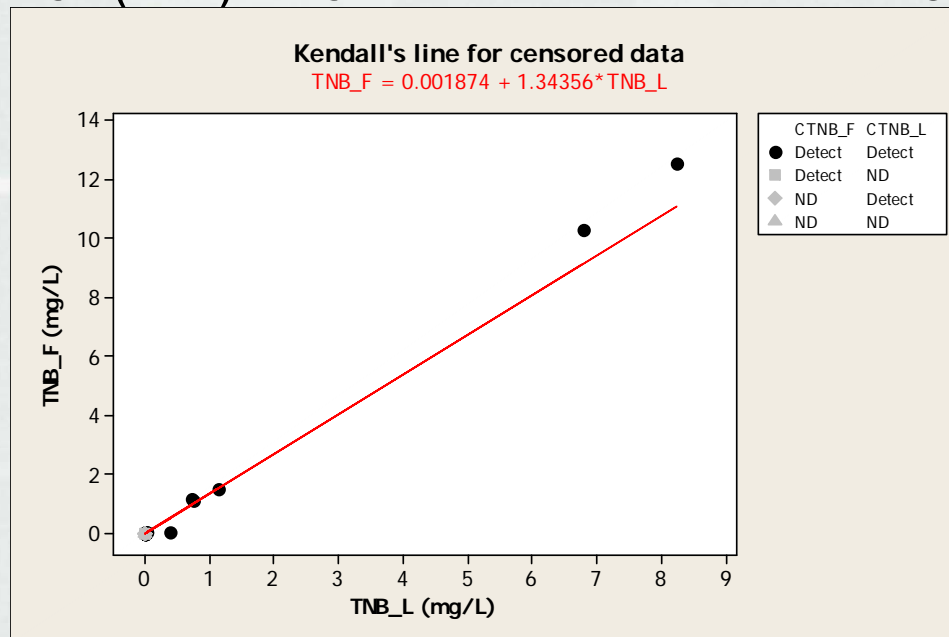
- 2,4-DNT results show excellent agreement
  - Limited concentration range and dataset due to several non-detects
  - Ordinary least squares fit:  $F = 0.88L + 0.0034$
  - Kendall-Theil (K-T) Line:  $F = 0.94 L + 0.000042$





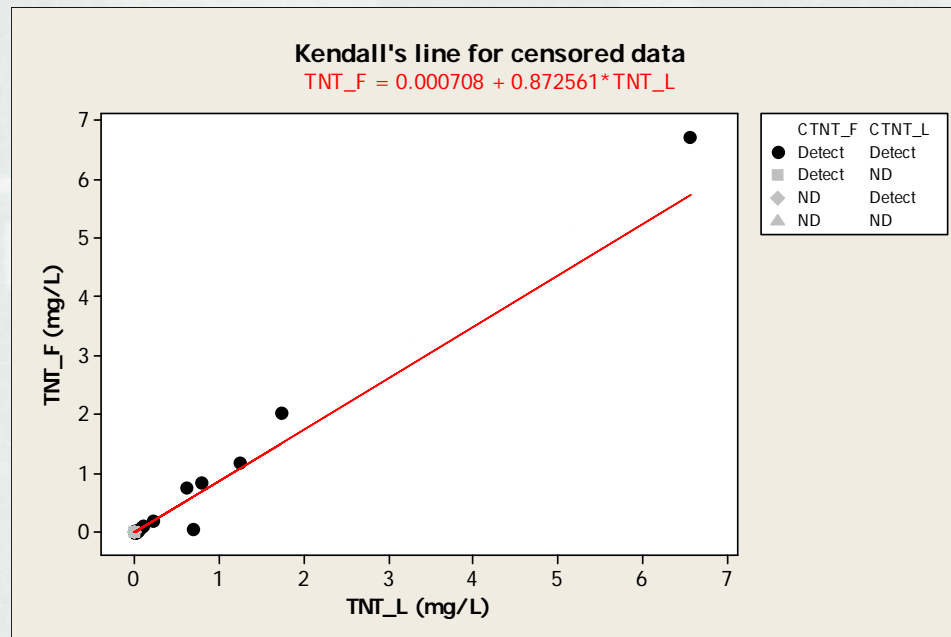
# Laboratory-Field Comparison

- TNB results show positive bias
  - ▶ Possibly owing to TNT interference
    - (similar mass signatures and little chromatographic separation)
  - ▶ TNT was often an order of magnitude or more higher than TNB
  - ▶ Ordinary least squares fit:  $F = 1.5L - 0.026$
  - ▶ Kendall-Theil (K-T) Line:  $F = 1.3 L + 0.0019$



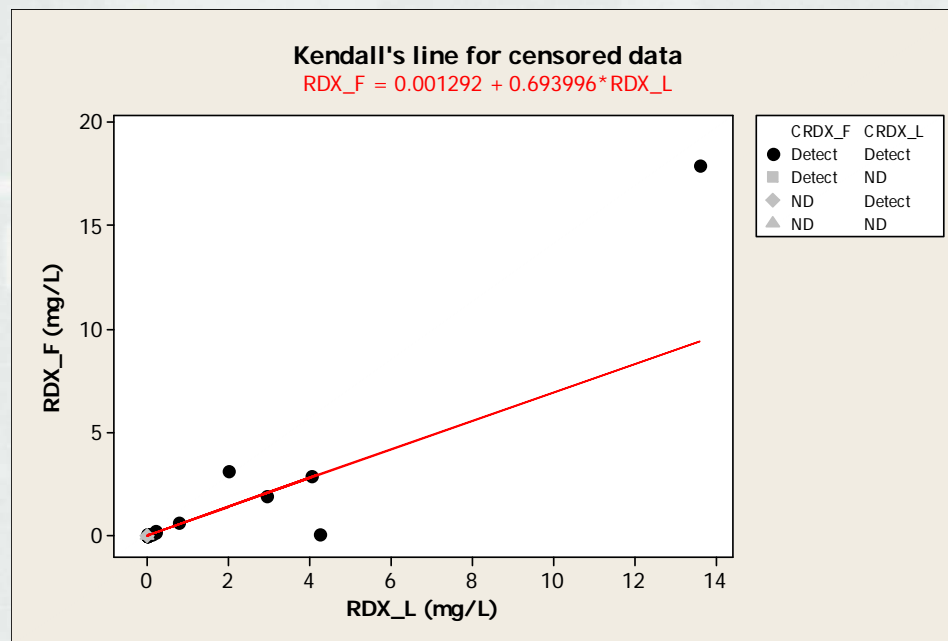
# Laboratory-Field Comparison

- TNT results show excellent agreement
  - ▶ Screening level data below approximately 0.05 mg/L
  - ▶ Ordinary least squares fit:  $F = 1.0L - 0.013$
  - ▶ Kendall-Theil (K-T) Line:  $F = 0.87 L + 0.00071$



# Laboratory-Field Comparison

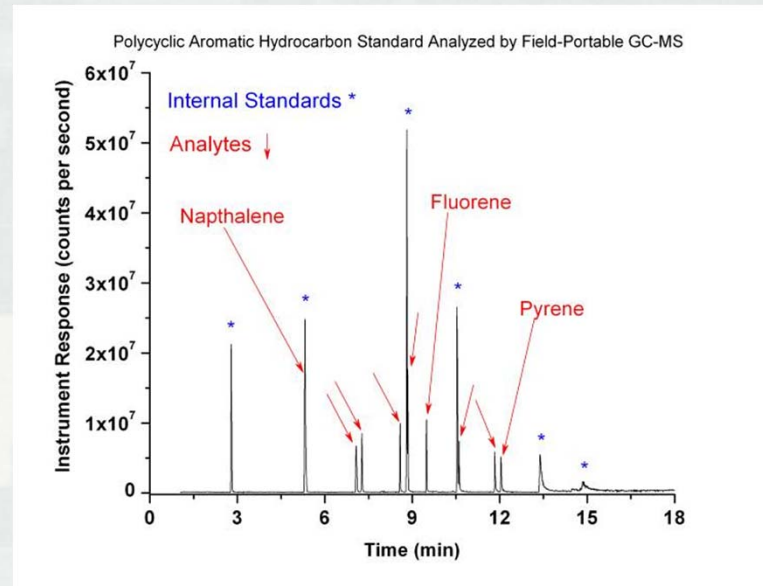
- RDX results had significant scatter
  - ▶ Stability of RDX during thermal separation likely limits utility
    - GC-ECD by Method 8095 also has RDX/HMX issues
  - ▶ Screening level data by field GC-MS
  - ▶ Ordinary least squares fit:  $F = 1.3L - 0.11$
  - ▶ Kendall-Theil (K-T) Line:  $F = 0.69 L + 0.0013$





# Other Applications

- PAH analysis in dredged material to identify oil spill residue during dredging
  - ▶ Deployed to Dredge BE Lindholm in August 2008
  - ▶ Analyzed water and sediment during operations
  - ▶ Near real time data lead to dredging decisions being made on scientific data rather than observations of 'sheen'



# Conclusions

- Field portable instrumentation can provide near real time analysis of munitions constituents in water
  - ▶ Quantitative Agreement for Most Analytes
  - ▶ TNB was positively biased
    - Possibly due to elevated TNT
  - ▶ RDX is difficult by thermal separation methods
    - Limited to screening level data without further refinement
  - ▶ Method development and instrument optimization are critical



# Future Work

- Delineation of PCB contamination at Anniston Superfund Site
  - ▶ Near real time analysis of sediments
- Other organic compounds
  - ▶ Pesticides, Gulf Oil Spill/PAH Analysis
- Further development of MIMS for direct analysis of water samples
  - ▶ No sample preparation/extraction needed





# Funding

- ESTCP
  - ▶ ER-0922
- Environmental Quality and Installation Long Term Monitoring



# Questions?

## Thank You

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[Anthony.J.Bednar@usace.army.mil](mailto:Anthony.J.Bednar@usace.army.mil)

[David.E.Splichal@usace.army.mil](mailto:David.E.Splichal@usace.army.mil)



# Laboratory-Field Cost Comparison

- Cost difference between the laboratory and field analysis
  - ▶ Breakeven point occurs at ~3.5 years
    - Assumes 12 5-day sampling trips/year and 25 samples analyzed per sampling trip. Total of 300 samples analyzed per year
  - ▶ Net present value (NPV) analysis
    - Savings of ~90K after 7 years (life expectancy of a field instrument)

